

Carbonation of Finnish magnesium silicates for CO₂ sequestration

Sebastian Teir, Sanni Eloneva, Soile Aatos, Olli-Pekka Isomäki,
Carl-Johan Fogelholm, Ron Zevenhoven

Carbonation of Finnish magnesium silicates for CO₂ sequestration

Sebastian Teir*, Post-graduate researcher

Helsinki University of Technology (TKK), Laboratory of Energy Engineering and Environmental Protection, P.O. Box 4400, FIN-02015 Espoo, Finland.

Phone: +358 9 451 3631, Fax: +358 9 451 3418, e-mail: sebastian.teir@tkk.fi

Sanni Eloneva, Post-graduate researcher

Helsinki University of Technology (TKK), Laboratory of Energy Engineering and Environmental Protection, P.O. Box 4400, FIN-02015 Espoo, Finland

Phone: +358 9 451 3631, Fax: +358 9 451 3418, e-mail: sanni.eloneva@tkk.fi

Soile Aatos, Geologist

Geological Survey of Finland, Eastern Finland Office, P.O.Box 1237, FIN-70211 Kuopio, Finland

Phone: +358 20 550 3778, Fax: +358 20 550 13, e-mail: soile.aatos@gtk.fi

Olli-Pekka Isomäki, Chief Mine Geologist

Outokumpu Mining Oy, Hituran Kaivos, Kummuntie 8, 85560 Ainastalo, Finland

Phone: +358 8 44 99 302, Fax: +358 8 44 99 230, e-mail: olli-pekka.isomaki@outokumpu.com

Carl-Johan Fogelholm, Professor

Helsinki University of Technology (TKK), Laboratory of Energy Engineering and Environmental Protection, P.O. Box 4400, FIN-02015 Espoo, Finland

Phone: +358 9 451 3631, Fax: +358 9 451 3418, e-mail: carl-johan.fogelholm@tkk.fi

Ron Zevenhoven, Professor

Åbo Akademi University, Heat Engineering Laboratory, Biskopsgatan 8, FIN-20500 Åbo, Finland

Phone: +358 2 215 3223, Fax: +358 2 215 4792, e-mail: ron.zevenhoven@abo.fi

ABSTRACT

Carbon dioxide capture and storage is considered as one of the main options for reducing atmospheric emissions of CO₂ from human activities, but in Finland no suitable geological formations are known to exist for CO₂ sequestration. Carbonation of Finnish magnesium silicates could provide a respectable reduction of CO₂ emissions in Finland, since Finland has a large abundance of mafic and ultramafic rocks, including serpentinites. In Eastern Finland alone there are about 121 km² of serpentinites, but the exact amounts and compositions of these are poorly documented. The serpentinites of Outokumpu-Kainuu ultramafic rock belt alone could be sufficient for storing 11 Mt CO₂ (about 1/7th of Finland's greenhouse gas emissions) each year for 200-300 years.

A high-temperature carbonation process could in theory produce excess heat suitable for power production. Therefore, one of the process routes being studied involves heat activation, hydration and gas-solid carbonation. Experiments with gas-solid carbonation of magnesium hydroxide have been performed using a pressurized thermogravimetric analyzer (PTGA). The results from the PTGA indicate that the carbonation reaction is controlled by product layer diffusion. The best carbonate conversion measured with the PTGA was 11 % in 6 h at 510 °C and 40 bar gas pressure (99 % CO₂, 1 % H₂O), while a chemical analysis of the partially carbonated sample showed a carbonate conversion of 60 %.

The most efficient carbonation processes suggested in literature involve leaching of silicate minerals and precipitation of carbonates or hydroxides. The efficiency for extracting magnesium ions from serpentinite was studied by leaching a characterized serpentinite batch in aqueous solutions of common acids and

* Corresponding author and principal presenter

bases. All acids tested (CH_3COOH , H_2SO_4 , HCl , HNO_3 and HCOOH) managed to extract a significant amount (3 – 26 %) of Mg from serpentinite in 1 h. None of the acids tested extracts Mg selectively from serpentinite: also Fe (2 – 16 %) and some Si (0 – 3 %) was extracted. Neither of the bases tested (KOH , NH_3 nor NaOH) managed to extract any significant content (> 0.3 %) of Mg, Fe or Si in 1 h. Higher temperature improved the magnesium and iron extraction efficiency of an aqueous solution of HNO_3 significantly. At 70 °C extraction temperature amorphous silica is formed, which can be separated from the solution by filtration. Precipitation was achieved by raising the pH of a filtered solution using NaOH , while CO_2 was bubbled through the solution. The precipitate contained mostly nitratine and some magnesium oxide carbonate.

1. INTRODUCTION

During the last century the global average surface temperature has increased by 0.6 °C, which appears to be the largest increase in temperature of any century during the past 1000 years (IPCC 2001b). The main cause for this seems to be anthropogenic (human-induced) emissions of heat-trapping gases, such as carbon dioxide (CO_2). The main source of anthropogenic CO_2 emissions during the past twenty years (about three-quarters) is due to the combustion of fossil fuel. According to IPCC, a combination of mitigation measures will be needed to achieve a stabilization of greenhouse gas concentration in the atmosphere, of which carbon dioxide capture and storage (CCS) is considered as one of the main options for reducing atmospheric emissions of CO_2 from human activities. Carbonation of silicate minerals has the highest capacity and longest storage time of CO_2 of the storage options currently known (Lackner 2003).

As an EU member, the Kyoto protocol binds Finland to reduce its greenhouse emissions to the level of 1990 (70.5 Mt) during 2008 – 2012. The target set for Finland appears to be quite challenging, since the production and utilization of power and heat is already remarkably efficient. Finland's annual greenhouse gas emissions have risen since 1990 and were during 2000 – 2004 at their highest almost 20 % larger than in 1990. It has been estimated that the Kyoto target for

Finland will be exceeded with 11 Mt each year (Ministry of Trade and Industry 2005). The locations and amounts of industrial (energy sector and industrial processes) CO_2 emissions in Finland are shown in Figure 1.

From Finland's perspective CCS does not provide an easy answer to decreasing CO_2 emissions, since no suitable geological formation appears to exist for sequestering CO_2 . The offshore oil and gas fields and saline aquifers located in the North Sea and Barents Sea appear to be the closest suitable CO_2 sequestration sites. Distances to these sites are approximately 500-1000 km (Koljonen et al. 2004). The only currently known CO_2 storage alternative for Finland is mineral carbonation, since Finland has widespread deposits of the minerals needed in the carbonation process.

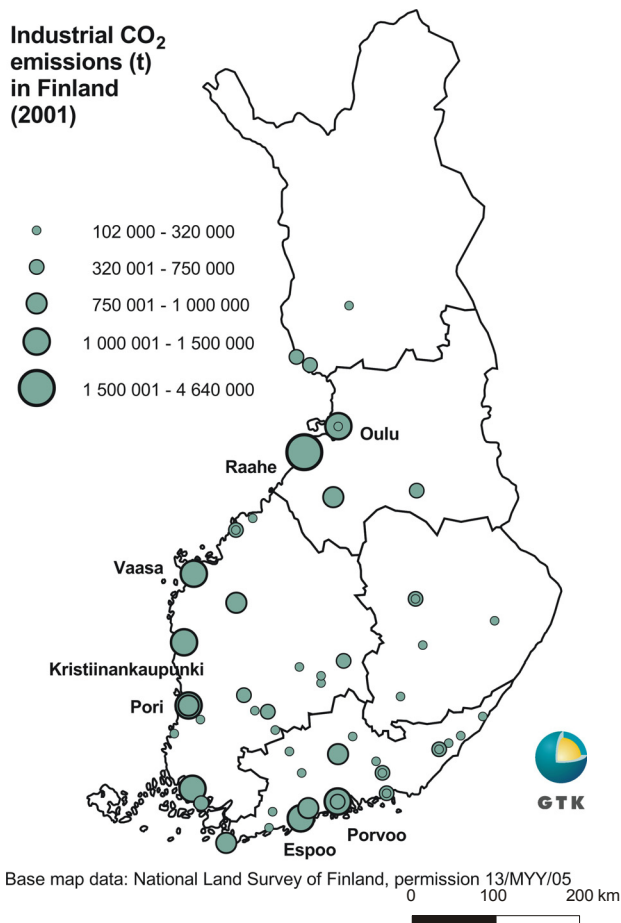
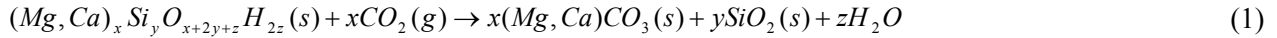


Figure 1. Industrial CO_2 emissions in Finland in 2001 (EU 2006).

Alkaline and alkaline-earth oxides, such as magnesium oxide (MgO) and calcium oxide (CaO), are present in large amounts and high concentrations in naturally occurring silicate rocks such as serpentine and olivine (Goff and Lackner 1998). Mineral carbonation produces silica (SiO₂) and carbonates that are stable over long time scales and can therefore be re-used as back-fillers in mines or for construction purposes. Although carbonates have industrial uses (Zevenhoven *et al.* 2006c), the utilization of carbonates is likely to be small relative to the production required for CO₂ sequestration. Since carbonation securely traps CO₂ in a carbonate compound more stable than CO₂ itself, there would be little need to monitor the disposal sites and the environmental risks would be very low (IPCC 2005). The net carbonation process using calcium- or magnesium silicates is presented in Equation 1 (Goldberg *et al.* 2001).



Except for the large and safe storage capacities, the exothermic nature of the net carbonation process is another benefit of mineral carbonation which motivates further research. Additional requirements for a commercial CO₂ storage process by mineral carbonation are mining, crushing and milling of the mineral-bearing ores, and their transportation to a processing plant that has access to concentrated CO₂ (from a capture plant). The natural process is very slow, which means that the carbonation process must be accelerated considerably to be a viable large-scale storage method for captured CO₂. Therefore, research in the field of mineral carbonation focuses on developing an accelerated carbonation process that is also energy-efficient.

This paper summarizes the status of the research of carbonation of magnesium silicates for long-term storage of CO₂ in Finland, focusing mainly on results from the last two years.

2. FINNISH MAGNESIUM SILICATES

The Finnish bedrock consists locally of rock types that contain abundantly Mg and Ca silicates, such as serpentine, pyroxenes and amphiboles. The most common Finnish Mg rich rocks are ultramafic intrusive or extrusive rocks, i.e. peridotites, dunites, hornblendites, pyroxenites and komatiites, and their metamorphic varieties, i.e. serpentinites, talc and asbestos rocks. Of these ultramafic rocks, the most interesting for CCS purposes are the serpentinites, because they consist mainly of serpentine (Table 1). Serpentines may contain about 40 % of MgO (Deer *et al.* 1982). Millions of tons of poorly documented *in situ* or hoisted serpentinite or tailed serpentine deposits situate mainly in central Finland.

Table 1. The mineral product mass of some common Finnish rock forming minerals needed for converting 10 Mt of CO₂ to carbonates.

Mineral name	or group	Approximate potential of a mineral to bind CO ₂ (kg/m ³) ¹	Mineral mass (Mt) needed to bind 10 Mt CO ₂
Olivine		2000	19
Pyroxene group		1300	27
Serpentine		1200	22
Amphibole		1100	29
group			
Talc		1100	25

¹ According to (Xu *et al.* 2001)

It has been estimated, according to the 1:100 000 scale geological mapping of Outokumpu-Kainuu ultramafic rock belt, that only in the Eastern Finland there are about 121 km² of serpentinites. About 30 % of this area has to be excluded because of an inconvenient location (watercourse, settled area or environmentally protected area). The effective sequestering capacity of these serpentinites is not known because of the considerable variation of the amount of pure serpentine in different serpentinite formations (Teir *et al.* 2006a). To achieve the reduction required by the Kyoto target set for Finland (about 11 Mt/a) by carbonation of serpentinite about 25 Mt/a of minerals would be required. Using these numbers, the serpentinites of Outokumpu-Kainuu ultramafic rock belt could theoretically be sufficient for 200-300 years of CCS processing, if low-emission technologies are being developed simultaneously (Teir *et al.* 2006a).

In Finland, minerals or rocks that could be suitable for binding CO₂ in economical amounts are situated especially in those ultramafic rock formations that have already been mined because of industrial minerals and metals, such as talc, soap stone, chromium and nickel. The total amount of hoisted rock in Finnish mines was about 31 Mt in 2004, of which about 11 Mt was from ultramafic deposits in general (Söderholm 2005). Some of the possibly suitable rocks for CO₂ capture are being constantly piled as barren rock or minerals dammed as tailings for waiting later use in the extractive industry (Figure 2). These minimum conditional resources of hoisted serpentinite and serpentinite (33-39 % MgO) in present Finnish Ni, Cr and talc mines (Hitura, Elijärvi, Horsmanaho and Lipasvaara) are about 29 Mt (Grönholm 1994, Rautiala 2004, Teir et al. 2006a).

One example is the Hitura ultramafic complex, which is composed of mainly dark, porous, fine-grained serpentinite. The main minerals are serpentinite (antigorite) 80 – 90 %, chlorite, calcite, and magnetite 7 – 9 % (Isohanni *et al.* 1985). A large part of the deposit is barren in nickel. Those parts of serpentinite rocks, which have had a low nickel grade are stored as waste rock at the mining site for future use. The waste stockpile now contains roughly 2.1 Mm³ of serpentinite. The total nickel ore hoist has been about 14 Mt, which has an average Ni content of 0.60 %.

The locations of already hoisted, piled or tailed ultramafic deposits are known, but their amount, mineralogy and mineral technical properties still need more clarification. The existing processing infrastructure and logistics make them easier to be considered as future raw material resources, than non-utilized *in situ* rock formations, if suitable industrial scale process technologies are developed for CCS purposes. The most suitable sources are serpentinite tailings deposits near industrial activities that emit CO₂ (Figure 2).

3. LEACHING AND CARBONATION OF SERPENTINITE

The most efficient processes suggested for carbonation involve leaching or dissolution of silicates in a liquid media and precipitation of magnesium or calcium as carbonates or hydroxides (Huijgen *et al.* 2003 and 2005). Most of these processes have been considered too expensive as a CO₂ storage process, since they require energy (for crushing, grinding or preheating) and /or chemical additives. However, very little experimental data on these processes are available.

Lackner (1995) suggested using HCl for recovering magnesium hydroxide from serpentinite to produce carbonates for CO₂ sequestration:

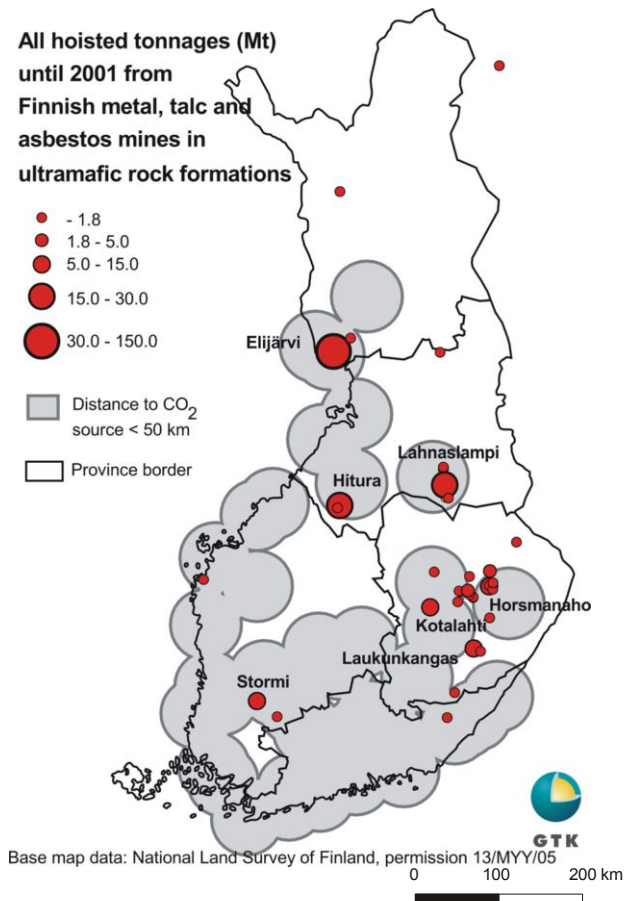
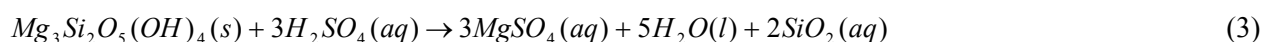


Figure 2. Possible resources of serpentinite in Finland (Puustinen 2003, EU 2006).

Wendt et al. (1998) concluded that the energy cost of the associated evaporation of water for acid recovery is too high for an economically viable implementation. According to Harris and Peacey (1992) 65-85 % Mg is released during 1 h reaction time in an HCl solution of 20-36 wt% at 65-100 °C (149-212 °F).

Park *et al.* (2003, 2004) studied the dissolution of serpentine in aqueous solutions of HCl, acetic acid, EDTA, orthophosphoric acid, and oxalic acid for a possible carbonation process. Park (2003) found that a mixture of orthophosphoric acid, oxalic acid, and EDTA gave the best dissolution of serpentine (measured as concentration of dissolved magnesium). However, using an acidic solvent for aqueous mineral carbonation, the overall carbonation process was limited by the rates of dissolution of CO₂ and dissociation of carbonic acid, rather than the dissolution rate of the mineral. By raising the pH of the solution to pH ~ 8.6 using NH₄OH, iron oxide was precipitated. By bubbling CO₂ through the solution, and increasing the solution to pH ~ 8.6 using NH₄OH, carbonation of MgCO₃·3H₂O occurred spontaneously.

Maroto-Valer (2005) recently patented a similar process for leaching Ca/Mg from silicate minerals, e.g. serpentine, using sulfuric acid for subsequent carbonation of MgSO₄:



According to this patent, maximum magnesium extraction achieved from serpentine was 71 % using sulfuric acid, 21% using hydrochloric acid, and 25% using phosphoric acid at 25 °C (77 °F) for 12 h.

According to a patent by Blencoe *et al.* (2004) silicate minerals can be decomposed using aqueous solutions of caustic soda (NaOH). In the patent, an aqueous solution of 30 – 80 wt-% NaOH is used for dissolving the silicates. However, slow carbonation rates are reported: a 90 % pure carbonate product can be achieved in 72 h at 15 bar and 200 °C (392 °F).

3.1. Methods

In order to find a suitable solvent for leaching magnesium from serpentine, the most common acids used in mineral processing (HCl, H₂SO₄, HNO₃) were tested alongside two common weak acids (HCOOH and CH₃COOH). Although acids are known to extract magnesium from magnesium silicates, bases are known to dissolve silicates and favor the formation of carbonates. Therefore, dissolution of serpentinite was also tested in solutions of NaOH, KOH, and NH₃.

Serpentinite from the stockpile of the Hitura nickel mine of Outokumpu Mining Oy, Central Finland, was selected for the experimental study. A batch of 7 kg serpentinite rocks was grinded and a particle size fraction of 74-125 µm was sieved from the ore batch. Samples of the grinded, unsieved batch and the sieved fraction were analyzed with XRD and XRF to compare how representative the sieved sample was for the unsieved serpentinite ore. For characterization, five samples of the sieved fraction were completely dissolved using a solution of 80 vol-% HCl, 16 vol-% H₃PO₄, and 4 vol-% HF, from which surplus of HF was eliminated using saturated boric acid (H₃BO₃). The solutions were analyzed with ICP-AES using two different wave lengths to give a more exact reference number for the concentrations of Mg, Si, Fe, Ca, Al, Ni, Mn, Cr, Cu, Co, and Ba in serpentinite. The carbonate (CO₃) content of serpentinite was determined using standard method SCAN-N 32:98.

In order to test the dissolution properties of the selected acids and bases 1 g of serpentinite was dissolved in separate 50 ml aqueous solutions of 1 M, 2 M and 4 M concentrations of one acid or base. The solutions were stirred at 1000 rpm at a room temperature of 20 °C (68 °F). The solutions were immediately filtered with 0.45 µm Pall GxP syringe filters 1 h after the addition of serpentinite. The filtered solutions were analyzed using ICP-AES for concentrations of Mg, Fe, Si. The experiments were repeated for each acid and base studied.

Based on the results from these tests, atmospheric batch experiments determining the temperature effect on leaching of magnesium from serpentinite were performed in a temperature-controlled bath with aqueous solutions of HNO₃ (50 ml HNO₃ and 200 ml H₂O). The solution was continuously stirred at 600 –

700 rpm using a magnetic stirrer. Temperature and pH were monitored inline. 1 l N₂/min was constantly fed through the solution to provide an inert atmosphere in the reactor glass (250 ml). The reactor glass openings had rubber corks sealing the electrodes and the gas outlet was equipped with a condenser to prevent loss of solution due to evaporation. Experiments were performed at 30 °C (86 °F), 50 °C (122 °F) and 70 °C (158 °F). When the temperature of the solution had stabilized after heat-up 5 g of serpentinite was fed through an inlet. Samples (10 ml) of the solution were taken 5 min prior to the batch feed, and 5 min, 20 min, 1 h and 2 h after the batch feed. The solution samples were immediately filtered with 0.45 µm Pall GxF syringe filters and analyzed using ICP-AES.

A first precipitation experiment was also performed, using a 100 ml of a filtered solution prepared by leaching 20 g serpentinite in a mixture of 200 ml HNO₃ and 300 ml H₂O for two hours at 70 °C (158 °F). The precipitation experiment was performed at 30-40 °C (86-104 °F) with a similar setup to that explained above with a flow of 1 l CO₂/min through the solution. Precipitation was promoted by slowly raising the pH of the solution by adding step-wise 2-5 ml of an aqueous NaOH solution (50 wt-% NaOH). Two hours after the last addition of the NaOH solution the mixture was filtered through a 0.45 µm Pall Supor filter paper and the filter residue was dried at 115-120 °C (239-248 °F) overnight. The dried filter residue was analyzed using XRD and XRF.

3.2. Results and discussion

A summary of the results from the serpentinite dissolution analyses and XRF-analysis of the sieved sample are shown in Table 2. The sieved fraction was very similar to the unsieved sample in respect to composition and crystal structure. The serpentinite samples consisted mostly of magnesite, iron and silicon in the form of serpentine (Mg₃Si₂O₅(OH)₄; chrysotile, lizardite and antigorite) and magnetite (Fe₃O₄). The serpentinite samples contained no carbonate. Major impurities were S, Ca, C and Cl (concentrations of 0.2 – 0.4 %). This serpentinite sample contained very low concentrations of valuable metals. Therefore, only the extraction of magnesium, iron and silicon was tested.

The results from extracting magnesium, iron and silicon from serpentinite in solutions of various acids and bases are shown in Figure 3 – Figure 5. The results are shown as mass of element dissolved in solution per mass of element in serpentinite (according to Table 2). All acids tested (CH₃COOH, H₂SO₄, HCl, HNO₃ and HCOOH) managed to extract a significant amount (3 – 26 %) of Mg from serpentinite in 1 h. According to the results presented in Figure 3 the solutions of H₂SO₄ were most efficient at extracting magnesium from serpentinite, followed by HCl, HNO₃, HCOOH and CH₃COOH (listed in order of descending magnesium extraction efficiency). Higher acid concentrations resulted in slightly more magnesium and iron ions dissolved, except for the solutions of CH₃COOH, which behaved more irregularly. None of the acids tested extracts Mg selectively from serpentinite: also Fe (2 – 16 %) and some Si (0 – 3 %) was extracted.

One interesting result is that no measurable amount of magnesium or iron (< 0.05 % extracted) had dissolved in any of the alkaline solutions tested (NaOH, KOH, and NH₃). No more than 0.3 % of the silicon in serpentinite was extracted using solutions of bases. It is possible that much longer residence time is required for extraction in alkaline solutions.

Table 2. Elemental analysis of serpentinite, 74-125 µm (only concentrations > 0.1 mg/g included from XRF-analysis).

Element	Average concentration (mg/g)	Method
Mg	218	ICP-AES
Si	116	ICP-AES
Fe	101	ICP-AES
S	4.8	XRF
Ca	3.4	ICP-AES
C	2.2	L.O.I.
Cl	2.1	XRF
Al	0.208	ICP-AES
Ni	0.205	ICP-AES
Ti	0.18	XRF
Mn	0.084	ICP-AES
Cr	0.074	ICP-AES
Cu	0.069	ICP-AES
Co	< 0.015	ICP-AES
Ba	< 0.005	ICP-AES

The effect of solution temperature on extraction efficiency was studied for aqueous solutions of HNO₃ (50 ml 65 wt-% HNO₃ and 200 ml H₂O). The result from the ICP-AES analyses of the solution samples taken during the course of the experiments are shown in Figure 6 – Figure 7. The figures show that extraction at higher temperatures in the HNO₃ solution raises the extraction efficiency of magnesium and iron from serpentinite significantly. Raising the temperature does not have a significant impact on Si extraction efficiency, but the rate of Si extraction is increased.

Based on these results a solution of 200 ml HNO₃ (65 wt-%) and 300 ml H₂O was prepared for the precipitation experiments by leaching serpentinite for two hours at 70 °C. After filtration a gel like residue was observed on the filter paper, which consisted mostly of amorphous silica (85 wt-% according to XRF analysis) and a small part of magnesium (5 wt-% MgO according to XRF analysis) as antigorite. The filtrate contained 7.9 g Mg, 1.8 g Fe and only 0.011 g Si per liter of solution (according to ICP-AES analysis), which shows that most of the Si precipitated. Precipitation of silica gel from the acidic solution seems to be promoted at higher temperatures, which also occurs when extracting calcium from calcium silicates in solutions of acetic acid at high solution temperatures (Teir *et al.* 2006b).

The filtrate was also used for a first precipitation test. After one hour with 1 liter of CO₂ per min bubbled through 95 ml of the solution no precipitate was visible, although 25 ml of a 50 wt-% NaOH solution had been added. After an additional 5 ml was added, a precipitate was immediately formed and the pH ascended fast from 0 to 9.5, after which the pH started to drop. No further NaOH was added. Two hours after the final addition of NaOH the pH of the solution had stabilized at 7.0. The filtered and dried precipitate contained 28 wt-% MgO, 5 wt-% Fe and more than 14 % Na₂O. Only 53 wt-% of the elements in the precipitate were identified, which indicates that the precipitate also contained crystal water. The carbon content was 2.7 wt-%, which corresponds to 14 wt-% CO₃, assuming that all the carbon in the sample was carbonate. Phases identified by the XRD analyses were nitratine, NaNO₃, and magnesium oxide carbonate, Mg₃O(CO₃)₂.

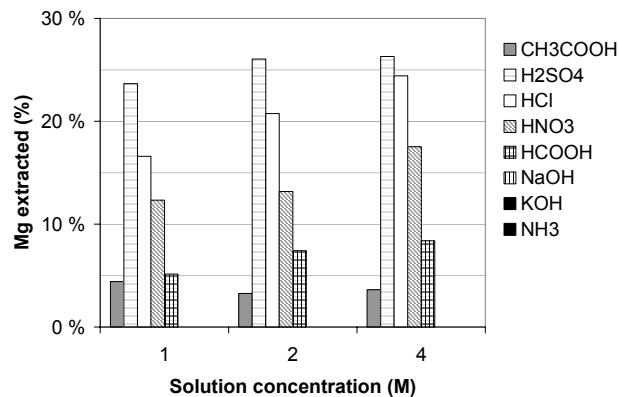


Figure 3. Relative mass of Mg extracted from serpentinite in 1 M, 2 M and 4 M concentrations of a selected acid or base (1 h, 20 °C).

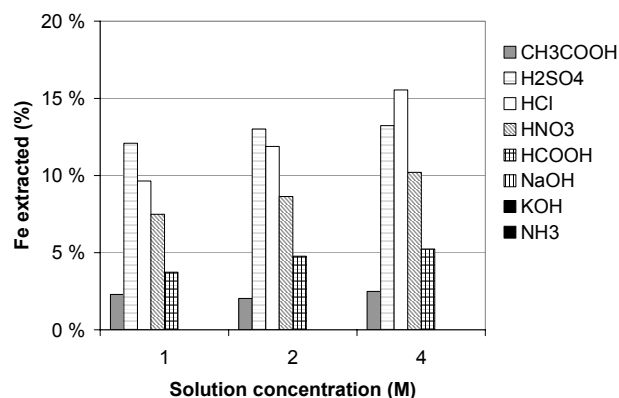


Figure 4. Relative mass of Fe extracted from serpentinite in 1 M, 2 M and 4 M concentrations of a selected acid or base (1 h, 20 °C).

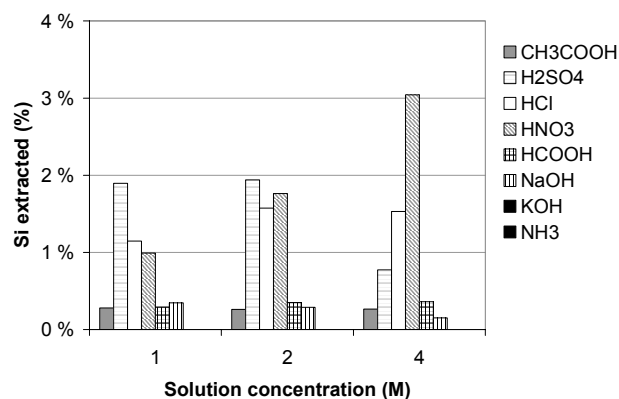


Figure 5. Relative amount of Si extracted from serpentinite in 1 M, 2 M and 4 M concentrations of a selected acid or base (1 h, 20 °C).

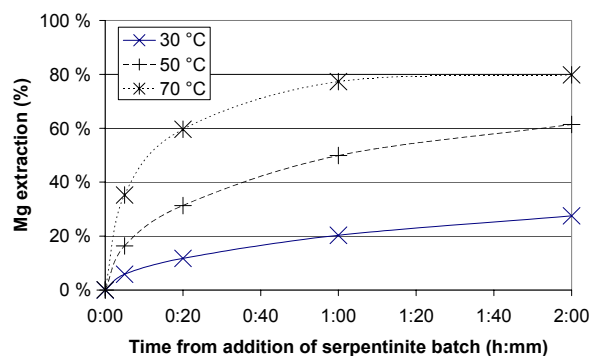


Figure 6. Relative mass of Mg extracted from 5 g serpentinite in solutions of 50 ml HNO_3 (65 wt-%) and 200 ml H_2O at 30 °C, 50 °C, and 70 °C.

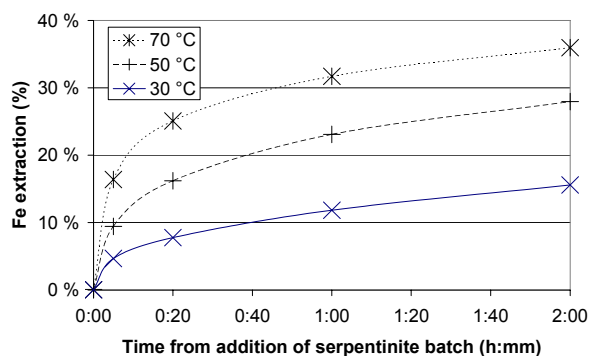


Figure 8. Relative mass of Fe extracted from 5 g serpentinite in solutions of 50 ml HNO_3 (65 wt-%) and 200 ml H_2O at 30 °C, 50 °C, and 70 °C.

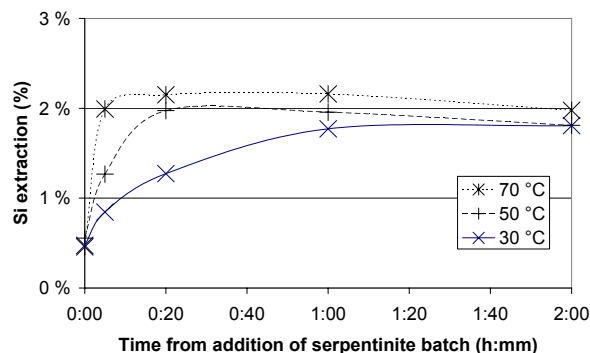


Figure 7. Relative mass of Si extracted from 5 g serpentinite in solutions of 50 ml HNO_3 (65 wt-%) and 200 ml H_2O at 30 °C, 50 °C, and 70 °C.

4. GAS-SOLID CARBONATION OF MAGNESIUM HYDROXIDE

Although most carbonation processes suggested require energy and additives, the overall chemistry of MgO-based silicate mineral carbonation is exothermic, suggesting that a properly optimized carbonation process could be operated with a negative overall energy input requirement. When operating the carbonation as a gas-solid process at a sufficiently high temperature and a certain minimum degree of conversion, the high temperature heat that is generated could possibly be used for process requirements or even electricity generation (Zevenhoven and Kavaliauskaite, 2004). However, it has been shown that the direct gas-solid carbonation of magnesium silicates is too slow for any technological application, suggesting that a staged process that extracts or activates the MgO is necessary. In a process that combines an endothermic MgO extraction step with an exothermic carbonation step the optimum temperatures for these steps will be different, and exergy analysis can be used to analyze the overall energy economy.

Another aspect here is whether to produce MgO or $\text{Mg}(\text{OH})_2$ from an MgO-based silicate. The scarce literature on MgO and $\text{Mg}(\text{OH})_2$ carbonation kinetics (Butt et al., 1996; Lackner, 2002; Béarat et al., 2002) suggests that the presence of H_2O increases the rate of carbonation of MgO and that the carbonation of $\text{Mg}(\text{OH})_2$ may be faster than for MgO, as illustrated in Figure 9 (Zevenhoven and Teir, 2004). Therefore, our research on gas-solid mineral carbonation addresses 1) chemical kinetics of MgO and $\text{Mg}(\text{OH})_2$ carbonation and the production of $\text{Mg}(\text{OH})_2$ from MgO-based minerals, primarily, serpentine, and 2) the process optimization of a three-step serpentine carbonation process such as schematically illustrated in Figure 10, that combines MgO extraction from serpentine, MgO hydration of $\text{Mg}(\text{OH})_2$, and $\text{Mg}(\text{OH})_2$ carbonation. A more detailed process optimization study is given elsewhere, showing also that the direct production of $\text{Mg}(\text{OH})_2$ from serpentine is not technically feasible at reasonable temperatures and pressures (Zevenhoven et al., 2006a).

The chemical kinetics of MgO and Mg(OH)₂ carbonation was studied using pressurized thermogravimetric analysis (PTGA). Samples of around 0.5 g of a 97.2 wt-% pure Mg(OH)₂, particle size 75 – 125 μm, were carbonated in 99 % CO₂ / 1 % H₂O (vol/vol) in a vertical PTGA system (reactor tube diameter 16 mm) at pressures up to 45 bar (so far). A cylindrical sample holder (diameter 10 mm, center stem 8 mm, leaving 1 mm for the sample layer) was used.

A first set of tests involved heat up to 700 °C (1292 °F) at 10 °C (18 °F) per minute and a holding time of 30 minutes at that temperature to produce MgO, followed by carbonation during a cooldown stage to 250 °C (482 °F) at 5 °C (9 °F) per minute. The second set of tests involved direct carbonation of Mg(OH)₂ at constant temperature and pressure, under conditions where MgO formation is thermodynamically prohibited, as illustrated by Figure 9.

Results from the tests based on wet chemical analysis of the samples before and after the test are collected in Table 3 and Figure 12 for the tests with MgO (calcined Mg(OH)₂) and Mg(OH)₂, respectively. The results in Table 3 show that increased pressure levels reduce the degree of MgO carbonation that is obtained. This is contrary to what might be expected from the fact that the reaction $\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3$ is thermodynamically limited by a minimum CO₂ partial pressure. MgCO₃ is stable at higher temperatures under higher CO₂ partial pressures, and chemical reaction kinetics are usually speeded up by increasing temperatures. Apparently the carbonation of MgO with CO₂ in the presence of small amounts of H₂O does not follow this general trend.

The results of the second test series (Figure 12) do show the expected increased level of carbonation with increasing pressures and temperatures. For a given pressure, temperatures were selected in the range $T = (0.85 \sim 0.95) \cdot T_{\text{eq}}$, where T_{eq} is the maximum temperature where MgCO₃ is stable at the given p_{CO_2} , to allow for some driving force - $\Delta G/T$ for the chemistry. Nonetheless, although for a given temperature a faster carbonation was obtained when pressure was increased, at a given pressure the carbonation rate appeared to decrease with temperature as a result of the thermodynamic limitation the equilibrium temperature T_{eq} presents. An example of XRD analysis of the resulting

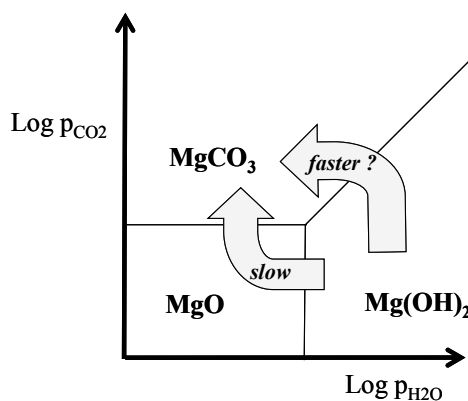


Figure 9. Phase diagram showing stability of MgCO₃, MgO and Mg(OH)₂ versus partial pressures of H₂O and CO₂.

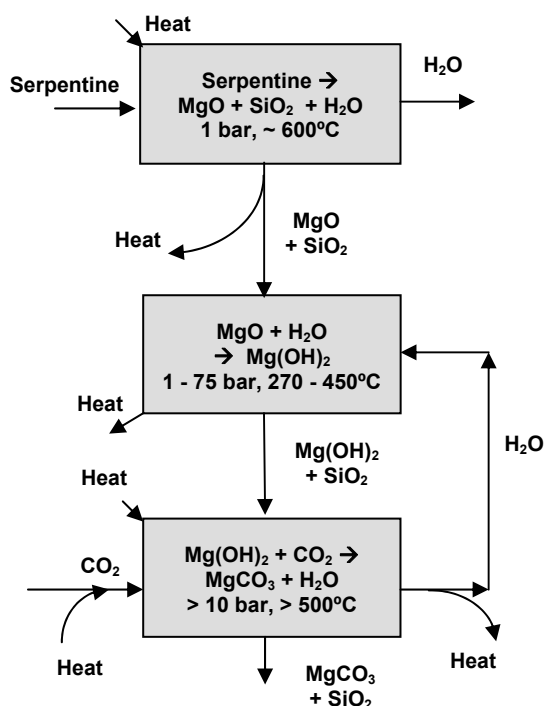


Figure 10. Process schematic for serpentine carbonation via MgO and Mg(OH)₂ production.

Table 3. Results of conversion of MgO to MgCO₃ during cooling from 700 to 250 °C (1292 to 482 °F) at 5 °C (9 °F)/ min in 99 %-vol CO₂ / 1 %-vol H₂O, for various pressures.

Pressure bar (psi)	Conversion %
1 (14.7)	5.6
5 (73.5)	4.4
12 (176)	3.1
20 (294)	3.4
35 (515)	2.9

products is shown in Figure 11, confirming a significant content of MgCO_3 in the material.

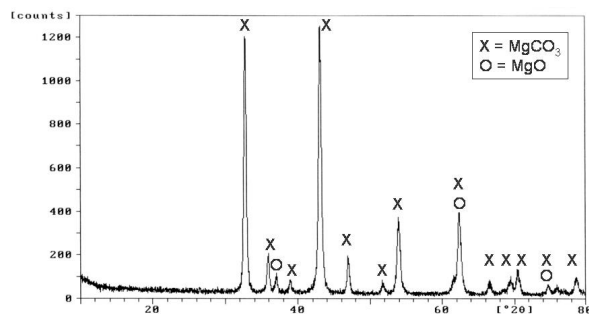


Figure 11. XRD analysis of a $\text{Mg}(\text{OH})_2$ carbonation test sample (45 bar, 525 °C).

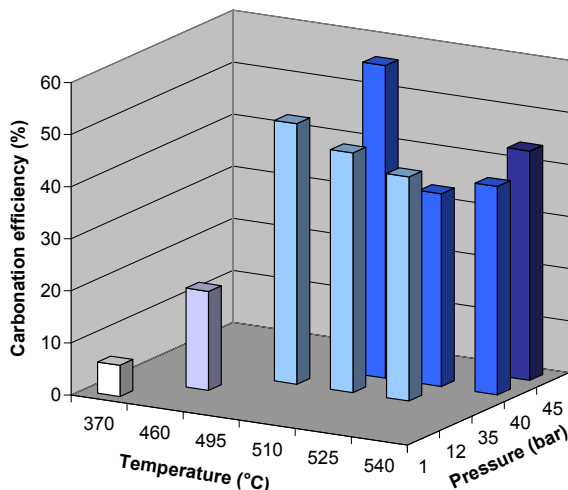


Figure 12. Results of conversion of $\text{Mg}(\text{OH})_2$ to MgCO_3 after 6 h for various temperature/pressure combinations in 99 %-vol CO_2 / 1 %-vol H_2O .

5. CONCLUSIONS

Technically, economically and environmentally feasible mineral carbonation processes are needed. For enhancing the economical output of the mineral carbonation recovery of metals, other valuable substances or energy, as well as logistics must be developed accordingly. The locations of already hoisted, piled or tailed ultramafic deposits in Finland are known, but their amount, mineralogy and mineral-technical properties still need more clarification. Our research on gas-solid carbonation has shown that carbonation of magnesium hydroxide is faster than carbonation of magnesium oxide. Raising the CO_2 pressure allows higher carbonation temperatures and improves the carbonation efficiency. Experiments with leaching of serpentinite have shown that magnesium can be extracted using common acids and bases, but also other elements will dissolve into the solution. However, more work is required to develop a continuous carbonation process.

FUTURE WORK

Minerals exploration and processing methods need further developing in relation e.g. to local industrial CO_2 emission sources after suitable carbonation technologies have been developed. Future work with carbonation of magnesium hydroxide will include more detailed analysis of the PTGA data and development of a kinetic model (see also Zevenhoven et al., 2006b). Also, carbonation tests with serpentine and $\text{Mg}(\text{OH})_2$ produced from serpentine at still higher, if possible also supercritical, carbon dioxide pressures will be carried out. Future work on leaching and carbonation of serpentinite will focus on finding a suitable solution and process option for producing magnesium carbonates from serpentinite. The precipitation of iron oxides and magnesium carbonates will be tested at atmospheric and pressurized conditions.

ACKNOWLEDGEMENTS

We thank Hannu Revitzer at the Laboratory of Physical Chemistry and Electrochemistry at TKK for performing part of the experimental and analytical work. We also thank Esko Pöyliö and Rita Kallio at Ruukki for providing us with XRF and XRD services. We thank the people working at the Laboratory of Energy Engineering and Environmental Protection and the Laboratory of Applied Thermodynamics at TKK for facilitating this work. We acknowledge the Nordic Energy Research, the National Technology

Agency of Finland (TEKES) and the Finnish Recovery Boiler Committee for financial support. Ron Zevenhoven acknowledges the Academy of Finland for an Academy Researcher position (2004-2005).

REFERENCES

BÉARAT, H., MCKELVY, M.J., CHIZMESHYA, A.V.G, SHARMA, R., CARPENTER, R.W., 2002. Magnesium hydroxide dehydroxylation/carbonation reaction processes: Implications for carbon dioxide mineral sequestration *J. Amer. Ceram. Soc.*, 85(4), 742-748.

BLENCOE, J.G., PALMER, D.A., ANOVITZ, L.M., BEARD, J.S., 2004. Carbonation of Metal Silicates for Long-Term CO₂ Sequestration; Patent application WO 2004/094043.

BUTT, D.P, LACKNER, K.S., WENDT., C.H., CONZONE, S.D., KUNG, H., LU., Y.-C., BREMSER, J.K., 1996. Kinetics of thermal dehydroxylation and carbonation of magnesium hydroxide. *J. Amer. Ceram. Soc.*, 79(7), 1892-1988.

DEER, W. A., HOWIE, R. A., ZUSSMAN, J., 1982. An Introduction to the rock-forming minerals, thirteenth impression, Longman, 528 p. ISBN 0-582-44210-9.

EU, 2006. European Pollutant Emission Register. Carbon dioxide emissions of Finnish facilities 2001. <http://www.eper.cec.eu.int>.

GOFF, F., LACKNER, K.S., 1998. Carbon Dioxide Sequestering Using Ultramafic Rocks. *Environmental Geosciences*, 5 (3), 89–101.

GOLDBERG, P., ZHONG-YING, C., O'CONNOR, W.K., WALTERS, R.P., 2001. CO₂ mineral sequestration studies in U.S. *In: Journal of Energy & Environmental Research*, Vol. 1, No. 1, U.S. Department of Energy. Available from: http://www.netl.doe.gov/publications/journals/jeer_toc.html [Accessed 9.11.2005]

GRÖNHOLM, S., 1994. Influence of mineral composition and microstructures on the mechanical properties of host rocks of the Kemi (Elijärvi) chromite deposit, Finland. Tutkimusraportti - Report of Investigation, 126.

HUIJGEN, W.J.J., COMANS, R.N.J., 2003. Carbon dioxide sequestration by mineral carbonation. Energy research Centre of the Netherlands (ECN), Report number ECN-C--03-016. Available from: <http://www.ecn.nl> [Accessed 27.7.2005]

HUIJGEN, W.J.J., COMANS, R.N.J., 2005. Carbon dioxide sequestration by mineral carbonation – Literature Review Update 2003-2004. Energy research Centre of the Netherlands (ECN), Report number ECN-C--05-022. Available from: <http://www.ecn.nl> [Accessed 3.11.2005].

IPCC, 2001b. Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC). Houghton, J.T., Ding, Y., Griggs, D.J., Noguer, M., van der Linden, P.J., Xiaosu, D. (Eds.). UK: Cambridge University Press.

IPCC, 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Approved and accepted by Intergovernmental Panel on Climate Change (IPCC) Working Group III and 24th Session of the IPCC in Montreal, 26 September 2005. Available from: <http://www.ipcc.ch/> [Accessed 1 November 2005]

ISOHANNI, M., OHENOJA, V., PAPUNEN, H., 1985. Geology and nickel-copper ores of the Nivala area. *Geol. Surv. Finland, Bull.* 333, 211-228.

- LACKNER, K., 2002. Carbonate chemistry for sequestering fossil carbon *Annu. Rev. Energy Environ.*, 27, 193-232.
- LACKNER, K.S., 2003. A guide to CO₂ sequestration. *Science*, 300, 1677-1678.
- LACKNER, K.S., WENDT, C.H., BUTT, D.P., JOYCE, E.L., SHARP, D.H., 1995. Carbon Dioxide Disposal in Carbonate Minerals. *Energy*, 20(11), 1153-1170.
- MAROTO-VALER, M.M., ZHANG, Y., KUCHTA, M.E., ANDRÉSEN, J.M., FAUTH, D.J., 2005. Process for sequestering carbon dioxide and sulphur dioxide. US Patent US2005/0002847.
- MINISTRY OF TRADE AND INDUSTRY, 2005. Lähiajan energia- ja ilmastopolitiikan linjauksia - kansallinen strategia Kioton pöytäkirjan toimeenpanemiseksi. National Climate and Energy Strategy. Available from: http://www.ktm.fi/energia-_ja_ilmastostrategia [Accessed 29.11.2005]
- PARK, A.-H.A., FAN, L.-S., 2004. CO₂ mineral sequestration: physically activated dissolution of serpentine and pH swing process. *Chemical Engineering Science*, 59, 5241-5247.
- PARK, A.-H.A., JADHAV, R., FAN, L.-S., 2003. CO₂ Mineral Sequestration: Chemically Enhanced Aqueous Carbonation of Serpentine. *Canadian Journal of Chemical Engineering*, 81, 885-890.
- PUUSTINEN, K., 2003. Suomen kaivosteollisuus ja mineraalisten raaka-aineiden tuotanto vuosina 1530-2001, historiallinen katsaus erityisesti tuotantolukujen valossa. Geological Survey of Finland, archive report. M 10.1/2003/3, 578 s.
- RAUTIALA, A., 2004. Talkin louhinnan serpentiinisivukiven ominaisuudet ja hyötykäyttö. Unpublished master's thesis. University of Oulu, 69 p.
- SÖDERHOLM, K., 2005. Tilastotietoja vuoriteollisuudesta 2004. Vuorimiesyhdistys r.y. Materia 2/2005, 45.
- TEIR, S., AATOS, S., KONTINEN, A., ZEVENHOVEN, R., ISOMÄKI, O.-P., 2006a. Silikaattimineraalien karbonoiminen hiilidioksidin loppusijoitusmenetelmänä Suomessa. Summary: Silicate mineral carbonation as a possible sequestration method of carbon dioxide in Finland. Vuorimiesyhdistys r.y. Materia 1/2006, 40-46.
- TEIR, S., ELONEVA, S., FOGELHOLM, C.-J., ZEVENHOVEN, R., 2006b. Dissolution of Steelmaking Slags in Acetic Acid for Precipitated Calcium Carbonate Production. Provisionally accepted for publication in *Energy*.
- WENDT, C.H., LACKNER, K.S., BUTT, D.P., ZIOCK, H.-J., 1998. Thermodynamic Calculations for Acid Decomposition of Serpentine and Olivine in MgCl₂ Melts, III. Heat Consumption in Process Design. Rep. LA-UR-98-4529, Los Alamos Natl. Lab., Los Alamos, NM, US.
- XU, T., APPS, J.A., PRUESS, K., 2001. Analysis of mineral trapping for CO₂ disposal in deep aquifers Lawrence Berkeley National Laboratory. Paper LBNL-46992 (July 20, 2001). <http://repositories.cdlib.org/lbnl/LBNL-46992>.
- ZEVENHOVEN, R., ELONEVA, S., TEIR, S., 2006a. Heat optimisation of a two-stage gas-solid mineral carbonation process for long-term CO₂ storage. Accepted for ECOS'2006, Aghia Pelagia, Crete, Greece, July 12-14, 2006.
- ZEVENHOVEN, R., ELONEVA, S., TEIR, S., 2006b. A study on MgO-based mineral carbonation kinetics using pressurised thermogravimetric analysis accepted for GHGT-8, Trondheim (Norway) June 19-22, 2006.

ZEVENHOVEN, R., ELONEVA, S., TEIR, S., 2006c. Chemical fixation of CO₂ in carbonates: Routes to valuable products and long-term storage. *In Press, Catalysis Today*.

ZEVENHOVEN, R., KAVALIAUSKAITE, I., 2004. Mineral carbonation for long-term CO₂ storage: an exergy analysis. *Int. J. Thermodynamics*, 2004; 7(1): 23-31.

ZEVENHOVEN, R., TEIR, S., 2004. Long-term storage of CO₂ as magnesium carbonate in Finland in: *Proc. of the 3rd Ann. Conf. on Carbon Capture and Sequestration*, Alexandria (VA), May 3-6, 2004.